

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **06-240392**

(43)Date of publication of application : **30.08.1994**

(51)Int.Cl.

C22C 19/07

C03B 37/04

(21)Application number : **05-212251**

(71)Applicant : **mitsubishi materials corp**

(22)Date of filing : **04.08.1993**

(72)Inventor : **MIHASHI AKIRA
SAHIRA TATEAKI
WAKITA SABURO**

(30)Priority

Priority number : **04356393** Priority date : **21.12.1992** Priority country : **JP**

(54) GLASS FIBER FORMING SPINNER MADE OF CO BASE ALLOY EXCELLENT IN WEAR RESISTANCE

(57)Abstract:

PURPOSE: To provide a glass fiber forming spinner made of a Co base alloy excellent in wear resistance and enabling a using service life over a long period.

CONSTITUTION: This glass fiber forming spinner is constituted of a Co base alloy having a compsn. contg., by weight, 0.22 to 1.2% C, 0.01 to 2% of one or more kinds of Si and Mn, 22 to 37% Cr, 5 to 15% Ni, 0.1 to 5% Hf and 5 to 12% of one or more kinds of Ta and Nb and furthermore contg., at need, one or more kinds among the following (a) to (c) of (a) 0.1 to 10% of one or more kinds of W and Mo, (b) 0.005 to 0.1% of one or more kinds of B and Zr and (c) 0.005 to 0.1% of one or more kinds among rare earth elements including Y, and the balance Co with inevitable impurities.

CLAIMS

[Claim(s)]

[Claim 1]By weight %, one sort in C:0.22 to 1.2%, and Si and Mn, or : [two sorts of] 0.01 to 2%, Cr: 22-37%, nickel:5-15%, Hf : One sort in 0.1 to 5%, and Ta and Nb, or : [two sorts of] 5 to 12%. An outstanding glass-fiber-forming spinner made from a Co base alloy of abrasion resistance constituting from a Co base alloy which has the presentation which it contains and the remainder becomes from Co and an inevitable impurity.

[Claim 2]By weight %, one sort in C:0.22 to 1.2%, and Si and Mn, or : [two sorts of] 0.01 to 2%, Cr: 22-37%, nickel:5-15%, Hf : One sort in 0.1 to 5%, and Ta and Nb, or : [two sorts of] 5 to 12%. An outstanding glass-fiber-forming spinner made from a Co base alloy of abrasion resistance constituting from a Co base alloy which has the presentation

which contains, and contains one sort in W and Mo, or : [two sorts of] 0.1 to 10% further, and the remainder becomes from Co and an inevitable impurity.

[Claim 3]By weight %, one sort in C:0.22 to 1.2%, and Si and Mn, or : [two sorts of] 0.01 to 2%, Cr: 22-37%, nickel:5-15%, Hf : One sort in 0.1 to 5%, and Ta and Nb, or : [two sorts of] 5 to 12%, An outstanding glass-fiber-forming spinner made from a Co base alloy of abrasion resistance constituting from a Co base alloy which has the presentation which contains, and contains one sort in B and Zr, or : [two sorts of] 0.005 to 0.1% further, and the remainder becomes from Co and an inevitable impurity.

[Claim 4]By weight %, one sort in C:0.22 to 1.2%, and Si and Mn, or : [two sorts of] 0.01 to 2%, Cr: 22-37%, nickel:5-15%, Hf : One sort in 0.1 to 5%, and Ta and Nb, or : [two sorts of] 5 to 12%, An outstanding glass-fiber-forming spinner made from a Co base alloy of abrasion resistance constituting from a Co base alloy which has the presentation which contains, and contains further : [one or more sorts of] 0.005 to 0.1% of rare earth elements containing Y, and the remainder becomes from Co and an inevitable impurity.

[Claim 5]By weight %, one sort in C:0.22 to 1.2%, and Si and Mn, or : [two sorts of] 0.01 to 2%, Cr: 22-37%, nickel:5-15%, Hf : One sort in 0.1 to 5%, and Ta and Nb, or : [two sorts of] 5 to 12%, Contain and further One sort in W and Mo, or : [two sorts of] 0.1 to 10%, An outstanding glass-fiber-forming spinner made from a Co base alloy of abrasion resistance constituting from a Co base alloy which has the presentation which contains one sort in B and Zr, or : [two sorts of] 0.005 to 0.1%, and the remainder becomes from Co and an inevitable impurity.

[Claim 6]By weight %, one sort in C:0.22 to 1.2%, and Si and Mn, or : [two sorts of] 0.01 to 2%, Cr: 22-37%, nickel:5-15%, Hf : One sort in 0.1 to 5%, and Ta and Nb, or : [two sorts of] 5 to 12%, Contain and further One sort in W and Mo, or : [two sorts of] 0.1 to 10%, An outstanding glass-fiber-forming spinner made from a Co base alloy of abrasion resistance constituting from a Co base alloy which has the presentation which contains : [one or more sorts of] 0.005 to 0.1% of rare earth elements containing Y, and the remainder becomes from Co and an inevitable impurity.

[Claim 7]By weight %, one sort in C:0.22 to 1.2%, and Si and Mn, or : [two sorts of] 0.01 to 2%, Cr: 22-37%, nickel:5-15%, Hf : One sort in 0.1 to 5%, and Ta and Nb, or : [two sorts of] 5 to 12%, Contain and further One sort in B and Zr, or : [two sorts of] 0.005 to 0.1%, An outstanding glass-fiber-forming spinner made from a Co base alloy of abrasion resistance constituting from a Co base alloy which has the presentation which contains : [one or more sorts of] 0.005 to 0.1% of rare earth elements containing Y, and the remainder becomes from Co and an inevitable impurity.

[Claim 8]By weight %, one sort in C:0.22 to 1.2%, and Si and Mn, or : [two sorts of] 0.01 to 2%, Cr: 22-37%, nickel:5-15%, Hf : One sort in 0.1 to 5%, and Ta and Nb, or : [two sorts of] 5 to 12%, Contain and further One sort in W and Mo, or : [two sorts of] 0.1 to 10%, : [one or more sorts of] 0.005 to 0.1% of rare earth elements which contain Y one sort in B and Zr, or : [two sorts of] 0.005 to 0.1%, An outstanding glass-fiber-forming spinner made from a Co base alloy of abrasion resistance constituting from a Co base alloy which has the presentation which it contains and the remainder becomes from Co and an inevitable impurity.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention shows the abrasion resistance outstanding to especially the high speed fluid of melting glass, and relates to the glass-fiber-forming spinner made from a Co base alloy to which the use over a long period of time is remarkably closed if possible.

[0002]

[Description of the Prior Art] Conventionally, generally, glass fiber inserts in a spinner the melting glass heated at about 1000 **, and carries out the high velocity revolution of this spinner at the number of rotations about 1700r.p.m., It is just going to be known well to be fabricated by making melting glass blow off from the fine pores of a large number radiately drilled in accordance with the side attachment wall of said spinner with a centrifugal force. Therefore, in above-mentioned glass-fiber-forming SUPINA. Many things made from a Co base alloy indicated, for example to JP,63-30384,B etc. are used from high temperature strength and elevated-temperature oxidation resistance, and abrasion resistance [further as opposed to the high speed fluid of melting glass] (only henceforth abrasion resistance) being required.

[0003]

[Problem(s) to be Solved by the Invention] On the other hand, although the above-mentioned spinner is strongly expected much more prolongation-of-life-ization of the use life from the field of FA-izing of glass fiber forming in recent years, and laborsaving, since the above-mentioned glass-fiber-forming spinner made from the conventional Co base alloy does not have enough abrasion resistance, the actual condition is resulting in a use life comparatively for a short time.

[0004]

[Means for Solving the Problem] Then, a result of having inquired this invention persons developing a wear-resistant outstanding glass-fiber-forming spinner from the above viewpoints, Are weight % (% shows weight % hereafter), and said spinner C:0.22 to 1.2% One sort in Si and Mn, or : [two sorts of] 0.01 to 2%, Cr: 22-37%, nickel:5-15%, Hf : One sort in 0.1 to 5%, and Ta and Nb, or : [two sorts of] 5 to 12%, It contains, necessity is accepted further and it is (a). One sort in W and Mo, or : [two sorts of] 0.1 to 10%, (b) One sort in B and Zr, or : [two sorts of] 0.005 to 0.1%, (c) If constituted from a Co base alloy which has the presentation which contains one or more sorts in (a) - (c) above, and the remainder becomes from Co and an inevitable impurity : [one or more sorts of] 0.005 to 0.1% of rare earth elements containing Y, After a glass-fiber-forming spinner made from a Co base alloy of this result possessed outstanding high temperature strength and elevated-temperature oxidation resistance, it showed much more outstanding abrasion resistance, and obtained a research result of demonstrating performance which continued and was excellent in a long period of time.

[0005] This invention is made based on the above-mentioned research result, and explains a reason which limited component composition of a Co base alloy which constitutes a spinner below as above-mentioned.

(a) Although dissolve on a base, and this is strengthened for CC ingredient and it acts to form carbide and to raise abrasion resistance, An effect of a request [at less than 0.22%] of the content to said operation was not acquired, but since toughness came to have fallen when the content exceeded 1.2% on the other hand, the content was determined as 0.22 to

1.2%.

[0006](b) Si and Mn -- since toughness came to have fallen when it contains for the purpose of deoxidation, and deoxidation with the content sufficient at less than 0.01% could not be performed, therefore the content exceeded 2% on the other hand, an ingredient of these determined the content as 0.01 to 2%.

[0007](c) Although form carbide in a CrCr ingredient, and abrasion resistance is raised for it and it acts to dissolve on a base and to raise elevated-temperature oxidation resistance, An effect of a request [at less than 22%] of the content to said operation was not acquired, but since it became as [fall / high temperature strength and toughness] when the content exceeded 37% on the other hand, the content was determined as 22 to 37%.

[0008](d) Although a NiNi ingredient acted to dissolve on a base and to raise high temperature strength, a high-temperature-strength improved effect of a request of the content at less than 5% was not acquired, but since much more improved effect did not show up with high temperature strength even if it made it contain exceeding 15% on the other hand, the content was determined as 5 to 15%.

[0009](e) Although form carbide in a HfHf ingredient, and abrasion resistance is raised for it and it acts to dissolve on a base and to raise elevated-temperature oxidation resistance, An effect of a request [at less than 0.1%] of the content to said operation was not acquired, but since toughness came to have fallen when the content exceeded 5% on the other hand, the content was determined as 0.1 to 5%.

[0010](f) Ta and Nb, although carbide is formed in an ingredient of these and it acts to dissolve on a base, to strengthen and have this and to raise abrasion resistance much more, A wear-resistant improved effect which the content excelled [% / less than 5] in a request was not acquired, but since toughness came to have fallen when the content exceeded 12% on the other hand, the content was determined as 5 to 12%.

[0011](g) W and Mo -- containing if needed, since form carbide in an ingredient of these, and abrasion resistance is raised for it and it acts to dissolve on a base and to raise elevated-temperature oxidation resistance, but. An effect of a request [at less than 0.1%] of the content to said operation was not acquired, but since toughness came to have fallen when the content exceeded 10% on the other hand, the content was determined as 0.1 to 10%.

[0012](h) B and Zr -- containing if needed, since an ingredient of these acts to strengthen and have the grain boundary and to raise high temperature strength, but. A high-temperature-strength improved effect of a request of the content at less than 0.005% was not acquired, but since toughness came to have fallen when the content exceeded 0.1% on the other hand, the content was determined as 0.005 to 0.1%.

[0013](i) Since a rare earth element containing the rare earth element Y containing Y acts to raise elevated-temperature oxidation resistance, contain if needed, but. When an improved effect of a request [at less than 0.005%] of the content to said operation was not acquired but the content exceeded 0.1% on the other hand, since fluidity and processability came to be spoiled, the content was determined as 0.005 to 0.1%.

[0014](j) If the content becomes to 4%, since it will not have any adverse effect on the characteristic, either, it may be made to contain positively in the range up to 4% in consideration of economical efficiency, although a FeFe ingredient is an ingredient usually contained as an inevitable impurity.

[0015]

[Example]Below, an example explains the glass-fiber-forming spinner of this invention concretely. The Co base alloy molten metal which had the component composition shown in Tables 1-4, respectively with the usual solution process is prepared, this -- ROSUTO wax precision casting -- diameter: -- 35 mmx thickness: -- this invention glass-fiber-forming spinner raw material by casting in a disc-like casting with the size of 5 mm. (It is hereafter called this invention spinner raw material) 1-40, and the comparison glass-fiber-forming spinner raw materials (henceforth a comparison spinner raw material) 1-8 were manufactured, respectively. Diameter:12 mmx length used for a creep-rupture examination and high temperature oxidation test which are done in order to evaluate high temperature strength and elevated-temperature oxidation resistance simultaneously: The molding by casting of the round bar material with the size of 120 mm was carried out. The comparison spinner raw materials 1-8 consist of a Co base alloy with the presentation which did not contain the ingredient of either of the alloy contents of the Co base alloy which all constitutes this or from which content (quantitative formula which gave * seal to the table) separated in the lower one from the scope of this invention.

[0016]Next, about the above-mentioned this invention spinner raw materials 1-40 and the comparison spinner raw materials 1-8, the central part of this -- thickness: -- it thinning down by cutting in 1 mm, a diameter:0.6mm hole being made in this thinning portion, and this being made into the bottom plate of the inside diameter:20mm crucible made from a Co base alloy, and within this crucible, Mean particle diameter : carry out air fusion of the soda glass which mixed 10-micrometer WC powder at a rate of 2 capacity %, and at 1075 **, where heating maintenance is carried out, said melting glass, adding the pressure of 3 atmospheres to said melting glass, blowing off melting glass from the hole of said crucible bottom plate, doing the melting glass jet examination which continues jet of this melting glass for 12 hours, and measuring the bore diameter after an examination from the upper part of said crucible, -- the bore-diameter rate of change from this measurement result -- namely [(bore diameter after an examination) - (bore diameter before an examination)] / (bore diameter before examination) x100 (%) was computed, and abrasion resistance was evaluated.

[0017]A creep-rupture examination begins to delete a specimen with a diameter:of parallel part diameter:7mmx parallel part length:32mmx zipper (screw) part12mmx overall-length:80mm size from the above-mentioned raw material, Using this specimen, it carried out among the atmosphere:atmosphere on condition of cooking temperature:960 ** and load stress:1 kg/[mm]², the fracture life was measured, and high temperature strength was evaluated.

[0018]A high temperature oxidation test begins to delete a specimen with a diameter:10mmx height:12mm size from the above-mentioned raw material, Using this specimen, cool after 2-hour maintenance at temperature:1100 **, and descaling is made into one cycle, this -- 12 cycle ***** -- things performed, the oxidation loss of the specimen after an examination was measured, the rate (oxidation loss rate) over the specimen weight before this measurement result blank test was computed, and elevated-temperature oxidation resistance was evaluated. These results were shown in Tables 5 and 6.

[0019]

[Table 1]

種 別		成 分 組 成 (重量%)									
		C	Si	Mn	Cr	Ni	Hf	Ta	Nb	選 択 成 分	Co+ 不純物
本 発 明 ス テ ィ ナ ー 素 材	1	0.224	0.52	—	26.0	10.4	1.1	7.9	—	—	残
	2	0.54	0.61	0.51	26.2	8.7	1.7	4.3	4.0	—	残
	3	1.18	—	0.72	26.7	9.8	2.9	2.1	6.3	—	残
	4	0.53	0.05	0.13	22.3	10.7	2.1	—	8.6	—	残
	5	0.47	0.04	0.10	36.6	12.0	2.5	7.2	1.3	—	残
	6	0.64	—	0.65	24.2	5.3	1.4	4.6	0.8	—	残
	7	0.57	0.31	0.22	32.6	14.9	1.3	7.0	—	—	残
	8	0.59	0.53	—	24.5	11.2	0.12	6.3	1.1	—	残
	9	0.61	0.23	1.01	35.7	9.9	4.9	—	6.8	—	残
	10	0.65	0.74	0.77	33.8	8.1	2.0	5.4	—	—	残
	11	0.63	—	0.41	30.3	8.2	2.1	11.7	—	—	残

[0020]

[Table 2]

顺 别	成 分						量 (重量%)			
	C	Si	Mn	Cr	Ni	Hf	Ta	Nb	遇 析 成 分	Co+ 不 溶 物
12	0.57	0.51	0.34	32.7	8.7	2.7	-	5.1	-	灰
13	0.61	0.20	0.54	29.9	10.4	2.7	-	11.4	-	灰
14	0.60	-	0.03	33.9	9.3	2.4	3.2	2.5	-	灰
15	0.65	0.10	0.56	34.6	8.9	2.3	5.9	5.7	-	灰
16	0.68	0.32	-	31.1	8.6	1.8	-	7.1	W:4.8	灰
17	0.51	0.18	0.07	33.8	9.6	2.0	4.1	2.3	Mo:0.8	灰
18	0.56	0.18	0.66	31.4	12.2	2.1	4.0	1.8	W:5.4, Mo:2.0	灰
19	0.67	-	0.21	33.5	10.5	1.0	5.3	-	B:0.03	灰
20	0.55	0.24	0.27	30.6	11.3	1.4	7.1	1.8	Zr:0.06	灰
21	0.62	0.15	0.30	24.9	7.8	1.1	6.9	0.9	B:0.01, Zr:0.05	灰
22	0.59	0.07	0.47	35.8	8.4	0.9	6.7	1.3	Ce:0.008	灰

[0021]
[Table 3]

顺列	成 分					组 成			(重量%)	
	C	Si	Mn	Cr	Ni	Hf	Ta	Nb	基 成 分	Co+ 不溶物
23	0.62	0.40	0.26	25.8	10.2	1.4	-	6.8	La:0.02, Nd:0.04	灰
24	0.58	0.15	0.29	32.4	10.1	2.1	6.8	0.2	Ce:0.001, La:0.01, Nd:0.04, Pr:0.02	灰
25	0.56	0.27	-	30.2	8.9	1.5	6.8	-	W:5.0, Zr:0.04	灰
26	0.51	0.29	0.35	26.7	8.9	0.8	5.5	0.5	W:5.8, Mo:1.5, B:0.02	灰
27	0.63	0.40	0.34	24.7	9.3	1.6	-	6.9	Mo:4.3, B:0.01, Zr:0.07	灰
28	0.64	0.13	0.51	26.2	9.1	2.1	7.1	2.0	W:4.1, La:0.02	灰
29	0.59	-	0.28	24.4	10.2	2.2	6.9	1.8	W:3.7, Mo:1.8, Nd:0.05, Pr:0.01	灰
30	0.57	0.11	0.64	25.9	9.5	2.4	-	7.8	Mo:2.7, Ce:0.02	灰
31	0.62	0.15	-	27.1	8.5	2.1	7.3	0.4	B:0.02, Ce:0.01	灰
32	0.60	0.28	0.66	28.8	8.4	1.0	7.7	-	Zr:0.05, La:0.06, Ce:0.01	灰
33	0.57	0.40	0.63	27.7	11.6	1.6	7.5	0.1	B:0.01, Zr:0.06, Nd:0.01, Pr:0.01	灰

[0022]
[Table 4]

種別	成分							組成 (重量%)		Co- 成分
	C	Si	Mn	Cr	Ni	Hf	Ta	Nb	組成成分	
34	0.66	0.21	0.16	29.6	12.2	1.8	7.2	0.2	W:4.1, B:0.02, Ce:0.03	炭
35	0.55	0.26	0.17	25.9	8.2	1.8	6.9	0.9	W:5.4, Mo:0.8, Zr:0.65, La:0.04	炭
36	0.56	0.17	0.87	32.9	7.9	2.1	6.1	0.8	Mo:2.6, B:0.01, Zr:0.64, Nd:0.04	炭
37	0.51	0.08	0.72	32.5	9.7	0.9	5.1	0.6	Y:0.08	炭
38	0.57	0.12	0.28	31.9	10.4	1.2	6.0	-	W:4.0, Y:0.06	炭
39	0.58	0.27	0.65	32.2	7.4	1.7	4.3	2.1	B:0.01, Zr:0.02, Y:0.05, La:0.01	炭
40	0.66	0.91	0.18	31.1	9.5	1.7	3.3	2.7	W:2.7, Mo:0.3, B:0.01, Y:0.09	炭
41	0.16*	0.43	0.61	27.3	7.6	2.3	5.6	1.1	-	炭
42	0.49	0.43	0.69	17.5*	9.0	2.8	2.8	6.6	-	炭
43	0.57	-	0.40	27.7	3.2*	4.0	4.1	2.2	-	炭
44	0.63	0.52	0.87	27.9	11.3	-*	4.8	2.1	-	炭
45	0.64	0.61	-	35.4	10.5	0.7	2.8*	-	-	炭
46	0.69	0.60	0.76	28.0	10.3	1.2	-	2.4*	-	炭
47	0.78	0.71	0.62	28.5	9.1	1.8	1.1*	2.0*	-	炭
48	0.15*	0.54	0.16	35.6	9.9	2.5	1.8*	-	-	炭

(*号: 本製鋼用外)

種 別	欠堅変化率 (%)	破断寿命 (時間)	酸化減速割合 (%)	種 別	欠堅変化率 (%)	破断寿命 (時間)	酸化減速割合 (%)
1	3.8	51.4	0.28	12	2.9	55.5	0.25
2	2.8	44.8	0.27	13	2.2	59.9	0.26
3	2.0	57.1	0.27	14	2.7	53.6	0.28
4	3.1	54.0	0.34	15	2.8	67.5	0.30
5	2.1	53.4	0.22	16	1.9	56.0	0.20
6	3.0	42.7	0.35	17	2.1	54.5	0.23
7	3.1	71.6	0.24	18	1.8	57.3	0.20
8	3.3	64.0	0.31	19	2.7	70.1	0.25
9	2.1	53.6	0.20	20	2.7	78.6	0.27
10	3.4	42.7	0.26	21	2.8	73.2	0.36
11	2.2	55.6	0.26	22	3.0	56.1	0.21

[0024]
[Table 6]

種 別	穴徑變化率 (%)	破斷壽命 (時間)	酸化減速割合 (%)	種 別	穴徑變化率 (%)	破斷壽命 (時間)	酸化減速割合 (%)
本 発 明 ス 比 較 ナ ー 絲 材	23	2.9	54.5	本 発 明 ス 比 較 ナ ー 絲 材	36	71.4	0.13
	24	3.0	57.7		37	51.8	0.21
	25	2.1	69.0		38	57.2	0.20
	26	1.8	70.2		39	69.8	0.21
	27	1.9	72.6		40	70.3	0.18
	28	2.0	59.6		1	49.2	0.31
	29	2.0	58.8		2	59.6	0.63
	30	1.9	62.2		3	21.5	0.30
	31	2.7	69.9		4	62.1	0.71
	32	2.8	69.5		5	25.8	0.27
ス 比 較 ナ ー 絲 材	33	2.7	71.7	ス 比 較 ナ ー 絲 材	6	20.3	0.39
	34	1.6	77.1		7	24.3	0.35
	35	1.5	70.0		8	24.0	0.38

[0025]

[Effect of the Invention] From the result shown in Tables 1-6, this invention spinner raw materials 1-40, To the outstanding abrasion resistance being shown after providing the high temperature strength and elevated-temperature oxidation resistance which were excellent in all, so that the comparison spinner raw materials 1-8 may see, If the component composition of the Co base alloy which constitutes this separates from the scope of this invention, it is clear to become the thing of the above-mentioned characteristics in which one of the characteristics was inferior at least. As mentioned above, since especially the glass-fiber-forming spinner of this invention has the

outstanding abrasion resistance and is excellent also in high temperature strength and elevated-temperature acid resistance, it demonstrates the performance which continued and was remarkably excellent in the long period of time when using, and shows a long use life.